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Final Report

INVESTIGATION OF CRYSTAL GROWTH PROCESSES

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ABSTRACT

A method for purification of KCl by anion and cation exchange has been developed. The crystalline product of the purification process and single crystals grown from this product were evaluated. This investigation shows that the method produces crystals superior to those currently available commercially. Optical data indicate the OH^-, Br^-, and I^- concentration has been reduced. Emission spectroscopy indicates the Na^+ content has been significantly reduced. Electrical conductivity measurements indicate that the divalent-ion concentration is comparable to that of 10-pass zone-refined material if compensation does not occur in either case. This work was reported at the 1962 International Color Symposium in Stuttgart, Germany.

An attempt was made to grow crystals from an H_2S solvent at high temperatures and pressures. To date these results have not met with success, but measurements of solubility show that it is a possible method for growing CdS and ZnS.

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I INTRODUCTION

The research being reported here was supported by Air Force Office of Scientific Research under Contract No. AF 49(638)-999 to investigate problems of crystal growth and to establish sources of high purity ionic crystals of technological importance.

The program consisted essentially of two parts. One part was a study of methods to produce ultrahigh purity ionic crystals and of measurements which can be used to evaluate and characterize these crystals. The second part was a study of crystal growth from nonaqueous solutions above their critical point but under sufficient pressure to maintain a reasonably high solvent density.

The study of methods to produce high-purity ionic crystals was chiefly concerned with the evaluation of procedures for purifying the raw material. Several methods were investigated but the one most successful (with KCl) consisted, in essence, of a prepurification through ion-exchange processes and subsequent production of single crystals in a crystal puller with refined temperature control. This work is described in Section II of the report.

The objective of the second part of the research program was to produce crystals from nonaqueous supercritical solutions. In this study hydrogen sulfide was selected as the most likely solvent and zinc sulfide and cadmium sulfide as the most interesting solutes. During the course of the investigation attempts, though not very successful, were made to measure solubility and solvent properties at the elevated temperatures and pressures used in the supercritical studies. This part of the investigation is described in Section III.

It is pertinent to note that this research program was curtailed due to the departure from the Institute of the principal investigator, Dr. W. J. Fredericks. It is felt that with additional time the study of crystal growth from supercritical solutions (described in Section III) would have been brought to a more successful conclusion.

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II EVALUATION OF PURIFICATION METHODS FOR POTASSIUM CHLORIDE

Potassium chloride was used as a typical ionic salt to test various methods of purification. Many of the standard methods of purification were examined and compared with a new ion exchange technique. The procedure followed was to pass a batch of KCl through a series of purifications and remove samples at each stage of the process and then to grow single crystals from these samples and compare the properties of the crystals with those from other stages of the same batch purification.

The purification procedures utilized were recrystallization, ion exchange, and sublimation.

In addition to selecting samples at each stage of the purification for crystal growth, portions of the sample were passed through the remainder of the purification in an attempt to detect which stages could be eliminated without affecting the quality of the finished crystal.

A.   Purification Methods

1.   Recrystallization

Analytical reagent grade potassium chloride was dissolved with 700-ml portions of deionized, heated water in a Pyrex beaker to form a saturated solution at approximately 80°C. The solution was then heated to boiling and filtered through Whatman No. 1 filter paper. The crystals which formed as the temperature of the filtrate decreased to approximately 70°C were separated by decanting the supernatant liquid and filtering it through glass wool; these crystals were discarded. After the filtrate had cooled to room temperature, crystals were separated by decanting the mother liquor. Excess mother liquor was removed and the crystals collected on Whatman No. 5 filter paper, using a Buchner funnel and water aspirator. After one-half hour the crystals were transferred to a Pyrex evaporating dish and dried overnight at 80°C. Five additions

of deionized water and KCl were added to the mother liquor of the
preceding batch before the mother liquor was discarded.

2. Ion Exchange

An exchange column was made of 1-inch I.D. Lucite tubing cemented
to a block of Lucite with a hole in it, and a smaller tube which was
connected to a stopcock with Tygon tubing. A 1-inch-diameter section
of polypropylene cloth was held in place at the bottom of the column
by a Lucite ring to prevent loss of the resin. Chelex 100, Bio-Rad
analytical grade chelating resin in the sodium form (50-100 mesh) was
slurried into the column to a bed volume of 200 ml.

The resin was converted to the hydrogen form by elution with 600 ml
of 0.5N HCl at a flow rate of approximately 20 ml/min. After rinsing
the column with 400 ml of deionized water, 600 ml of 0.5N KOH was passed
through the column from the bottom to prevent breakage of the column by
the potassium form due to swelling of the resin. The column was rinsed
from the bottom with 800 ml of deionized water.

A 20 percent solution of potassium chloride was passed through the
column at a flow rate of 20 ml/min. The first 400 ml of effluent was
discarded. Thereafter the first 200 ml of effluent was discarded each
day that the column was used. The remaining effluent was concentrated
by heating 1 liter of the solution in a 2-liter Pyrex Erlenmeyer filter
flask connected to a water aspirator. When the volume had been reduced
to approximately half of the original volume, the solution and crystals
were allowed to cool to room temperature. The crystals were separated
by decanting the supernatant liquid and then were collected and dried
on Whatman No. 5 filter paper in a Buchner funnel for one-half hour
using a water aspirator. The crystals were then transferred to a Pyrex
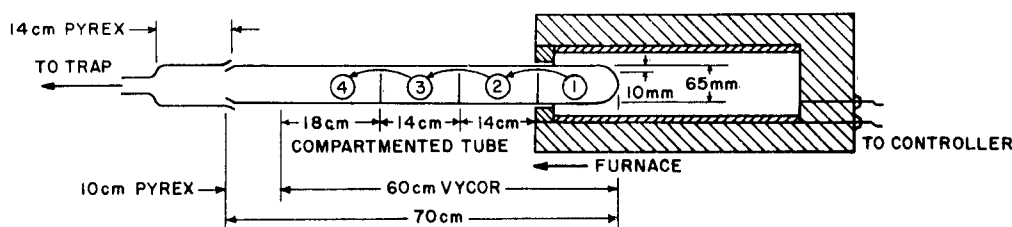crystallizing dish and dried overnight at 160°C.

Bio-Rad analytical grade anion exchange resin AG 2-X10 in the
chloride form (50-100 mesh) was slurried into a column (similar to the
one described above) to a bed volume of 200 ml. One liter of deionized

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water was put through the column at a flow rate of 20 ml/min before 450 ml of a 20% KCl solution was put through. After this treatment the anion exchange column was placed in series with the chelating resin column. Four hundred ml of KCl solution was put through the two columns before the effluent was collected for the recovery of the dissolved KCl as described above.

3.   Sublimation

Between 250 and 350 grams of KCl to be purified by sublimation was placed in the first chamber of the Vycor tube shown in Fig. 1. The tube was evacuated to 1×10^{-6} mm Hg pressure before it was heated. The first chamber was kept at a temperature of 400°C with continuous pumping overnight and chambers 2, 3, and 4 were heated to slightly more than 100°C with a heating tape. A stainless steel dry ice-acetone trap was then included in the system. The dry ice-acetone trap connected to an oil diffusion pump through a baffled silver-plated brass liquid nitrogen trap. The pressure measured between the two traps was 5×10^{-7} mm Hg during operation of the apparatus.

To effect transfer, the temperature at chamber 1 was increased to approximately the melting point of KCl so that KCl was transferred to chamber 2 in approximately 12 hours. The furnace was then moved to heat chambers 1 and 2 and thus to effect the transfer of KCl to chamber 3. The KCl was finally transferred to chamber 4.

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FIG. 1   SUBLIMATION APPARATUS

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The sublimed KCl in chamber 4 on the pump side of the glass joint and the 3-cm portion of the KCl in chamber 4 closest to the furnace were discarded. The yield of purified material was approximately 75%.

B. Crystal Growth

The products from the various stages of the purification procedure were grown into single crystals under as nearly identical conditions as possible.

A Kyropoulos method was used to pull single crystals from a melt. The apparatus used for this is shown in Fig. 2. This small puller
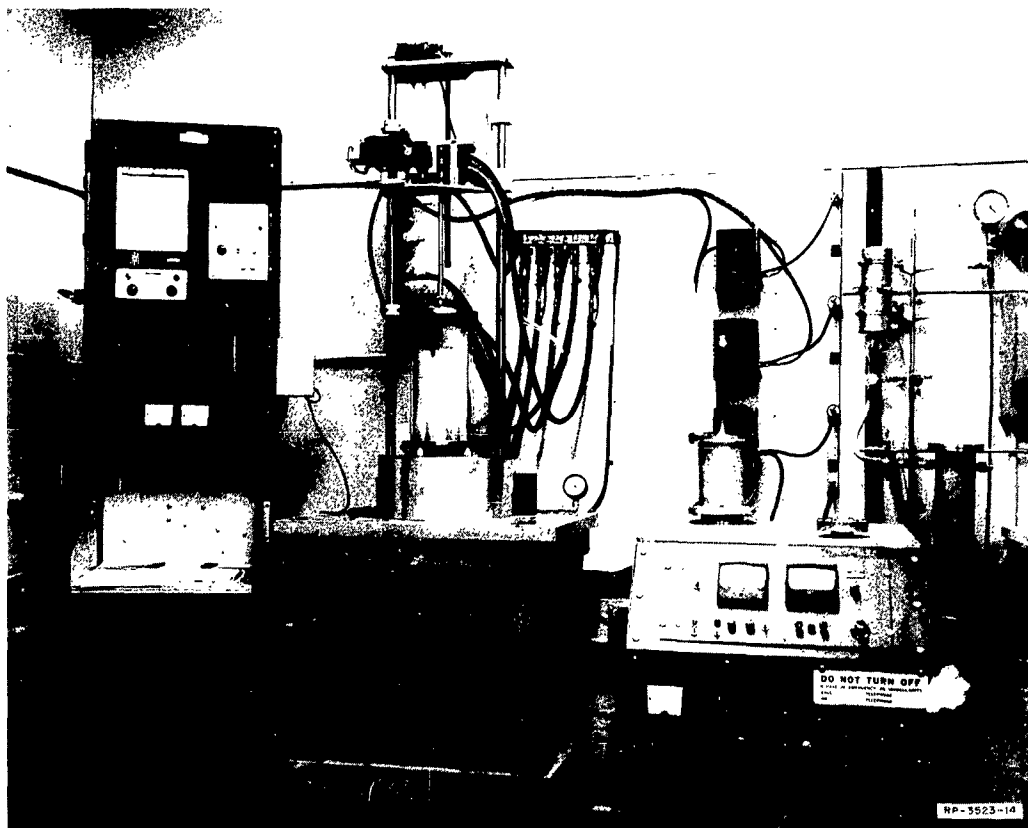

FIG. 2 APPARATUS FOR PULLING SINGLE CRYSTALS

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allowed the use of relatively small quantities of purified salt. The puller was designed so that the graphite heating element and its graphite supports were the only parts of the puller at high temperature which were exposed to the melt. The other parts of the system (which were in the controlled atmosphere region of the puller) were the cold finger of rhodium-plated nickel, a tantalum heat shield outside the graphite heating element, the water-cooled copper electrical connectors to the graphite supports for the heating element, a rhodium-plated nickel heat shield, a rhodium-plated stainless steel heat shield, the Pyrex outer wall, and the water-cooled end plates. The vacuum-tight seal between the end plates and the Pyrex wall was made by a neoprene O-ring. The sliding seal between the nickel crucible support and the pulling rod was a greaseless neoprene Wilson seal.

The temperature of the KCl melt was controlled by a "blind system." The temperature near the outside of the graphite heating element was sensed with a chromel-alumel thermocouple. The output of this couple was compared with a reference voltage. The reference signal was supplied from a LeCarbon Air Cell, a step-switch voltage divider and 10-turn potentiometer. The error signal between the set reference voltage and the sensing thermocouple was amplified by a Leeds-Northrup null detector and used to operate a C.A.T. controller which in turn regulated the power input to the furnace through a magnetic amplifier and saturable reactor.

Purified KCl was placed in a 1-9/16-inch diameter by 2-5/8-inch crucible of UT-6 graphite (maximum ash 0.005%) which had been rinsed with electronic grade acetone. The crucible was placed inside the graphite heater which was inside a tantalum shield. Two heat shields of rhodium-plated nickel and stainless steel respectively were placed outside the tantalum shield. The system was evacuated to 1×10^{-5} mm Hg and the temperature slowly increased to about $400^{\circ}C$ and maintained for 16 hours. After this period of heating and pumping, the pressure was approximately 2×10^{-6} mm Hg. Enough argon was introduced to produce a pressure of 1 atmosphere when the furnace was at the melting point

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of KCl. The temperature was then increased to melt the KCl. Additional purified KCl was added, if necessary, after allowing the crucible to cool and the above procedure repeated.

It was advisable to allow at least two hours for the system to come to thermal equilibrium before attempting to pull a crystal. The seed crystal (Isomet or Harshaw) was immersed in the melt and was pulled at a rate of 2 centimeters per hour while rotating counterclockwise at 3.25 revolutions per minute. The crucible was rotated at 2.80 revolutions per minute. All crystals were grown under conditions similar to those outlined above.
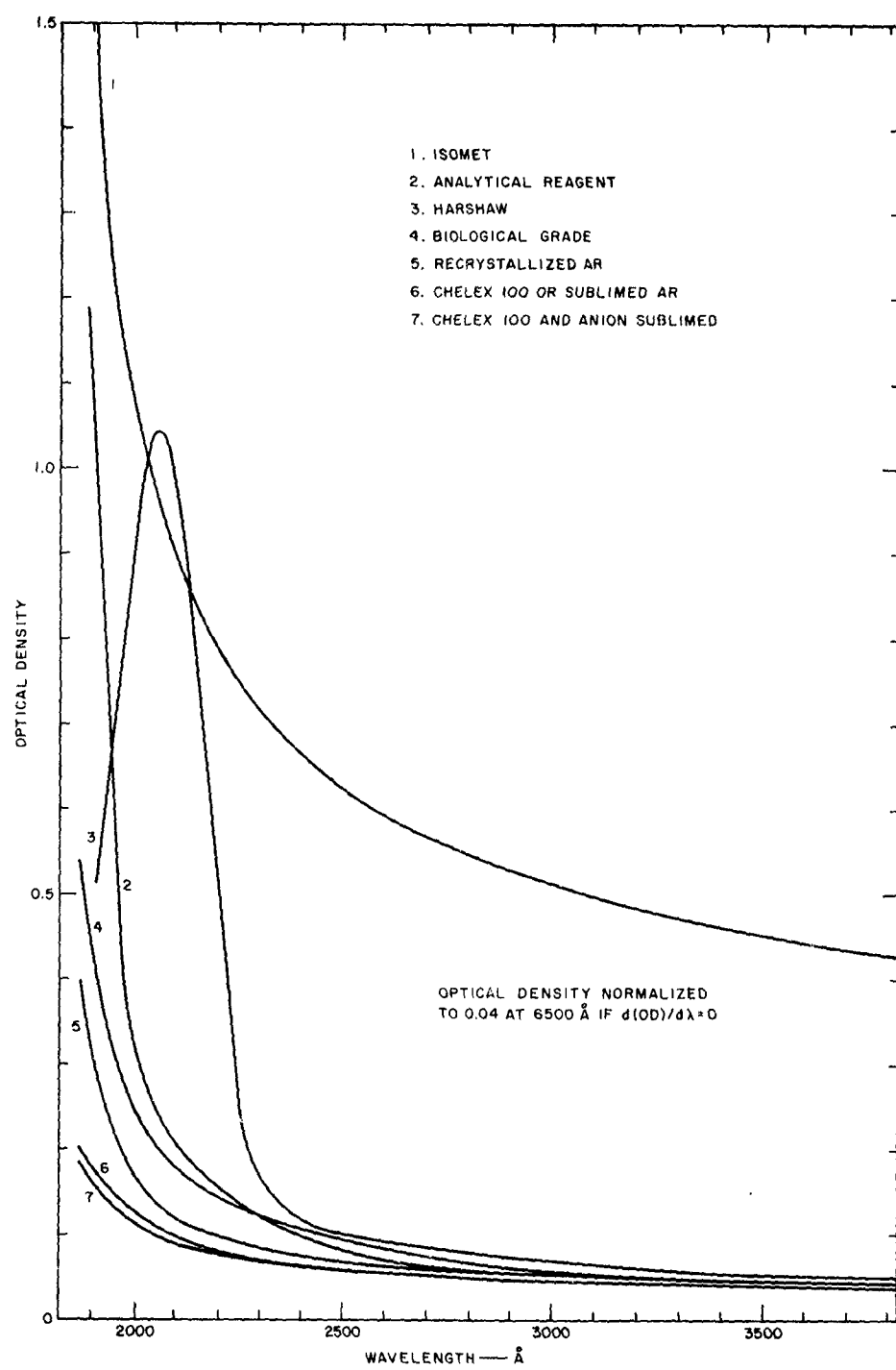
C.   Crystal Evaluation

1.   Optical Absorption

Many impurities introduce well-defined absorption bands on the long wavelength side of the fundamental absorption edge of KCl. Certainly the bands due to cation impurities should not be detectable in the crystals and were not. A band at 2060A occurs in KCl and is usually assigned to a hydroxide ion impurity or to oxygen. This band is usually evident in crystals which were grown in air or from KCl which was not completely dried.

The crystals produced in this program were examined in the spectral region from 1865A to 10,000A with a Cary Model-14 recording spectrometer.

A cross section from the last portion grown of each single crystal boule was mounted over a 1/4-inch-diameter aperture, on a section of 0.5-inch blackened aluminum angle for these measurements. None of the samples examined showed any absorption bands due to cation impurities. Only Harshaw crystals possessed the 2060A band. The other commercial crystal, Isomet, exhibited an abnormally large amount of scattering and the slope of O.D. with wavelength did not approach zero over the entire wavelength range studied. All other crystals were normalized to O.D. = 0.04 cm^{-1} at 6500A. These data are shown in Fig. 3. Unfortunately the

1. ISOMET
2. ANALYTICAL REAGENT
3. HARSHAW
4. BIOLOGICAL GRADE
5. RECRYSTALLIZED AR
6. CHELEX 100 OR SUBLIMED AR
7. CHELEX 100 AND ANION SUBLIMED

OPTICAL DENSITY NORMALIZED
TO 0.04 AT 6500 Å IF $d(OD)/d\lambda = 0$

OPTICAL DENSITY

WAVELENGTH —— Å

RC-3523-3

FIG. 3   ABSORPTION SPECTRA OF SINGLE CRYSTALS OF KCl

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Cary spectrophotometer cannot operate in the wavelength region of the absorption edge in KCl. But the absorption below 2000A is appreciably less in the crystals grown from salt purified by ion exchange methods than in all other crystals. This lack of a large "long wavelength tail" may indicate a low concentration of bromide and iodide ion in these crystals.

2. Ionic Conductivity

Ionic conductivity was once considered the best criteria of freedom from polyvalent ions in alkali halides. However, it has recently been shown that compensation of polyvalent cations by polyvalent anions can occur. Thus the estimate of impurity content from conductivity data may be quite unreliable. However, while the calculation of the divalent-ion content from specific conductivity may not be useful, it is interesting to compare such data for crystals considered to be very pure with conductivity data on the better crystals grown in this work.

The direct current conductivity of the crystals grown from purified KCl was measured with a Keithly electrometer Model 200B. The polarity of the potential across the crystal was reversed every 1.25 sec to reduce polarization. The current to the electrometer was also simultaneously reversed, and the average current was used to determine the specific conductivity in the temperature range from 190°C to 520°C. The reversing and calibration circuits are shown in Fig. 4. The conductivity apparatus was calibrated by substitution of resistors accurate to 1% on S_2 of the circuit in Fig. 4.

Gold was evaporated on the crystal sections to provide contact between the crystal and the graphite rods which were used as the electrical leads. The crystal and graphite rod were in the quartz cell inside the furnace. A small flow of argon was passed through the cell to provide an argon atmosphere during the measurements. The conductivity cell is shown in Fig. 5.
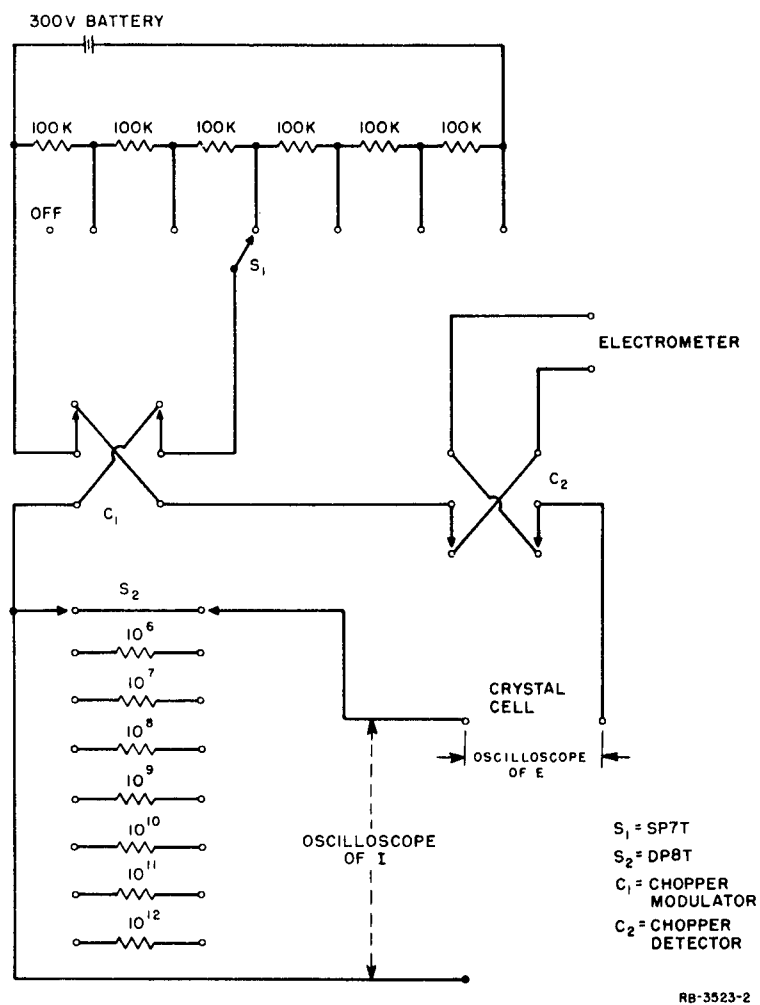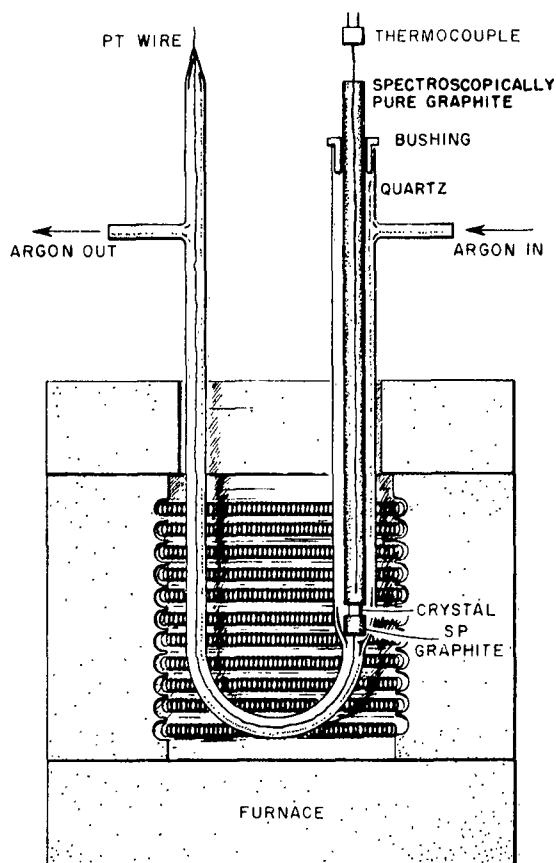
FIG. 4   CIRCUIT FOR CONDUCTIVITY MEASUREMENTS

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PT WIRE

THERMOCOUPLE

SPECTROSCOPICALLY
PURE GRAPHITE

BUSHING

QUARTZ

ARGON OUT

ARGON IN

CRYSTAL

SP
GRAPHITE

FURNACE

RA-3523-5

FIG. 5 CONDUCTIVITY CELL

The specific conductivities for two samples of anion and cation purified KCl single crystals and one from a sample of the same raw material sublimed are shown in Fig. 6. Similar data obtained by Gründig[1] on zone-refined crystals are also included.

Comparison of measurements of specific conductivity of these crystals with Gründig's show them to be approximately equal to his 10-zone-pass crystals. It is interesting that the activation energy for conduction is in such good agreement with his data.

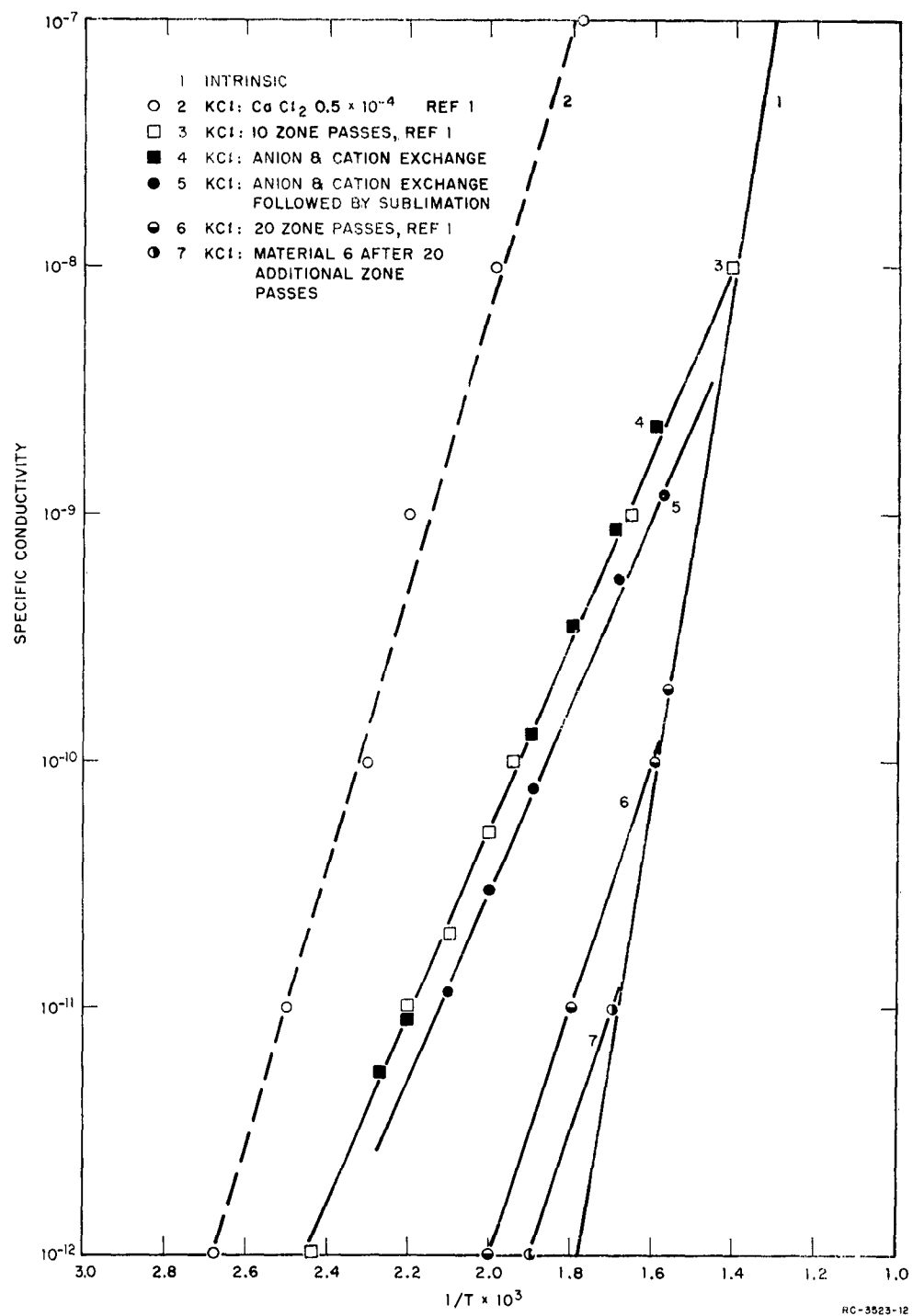[1]Hellmot Gründig, Z. Für Physik 158, 577 (1960)

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FIG. 6 SPECIFIC CONDUCTIVITY OF KCl CRYSTALS

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3. Spectrographic Analysis

The high-pressure-argon, arc-emission spectrographic analysis was carried out by Combustion Engineering, Inc. at our request. The origin and history of the samples were unknown to them. Duplicates of various samples were included as well as a few intentionally doped samples. In all cases they were successful in detecting the identity of the dopant. The comparison of duplicate samples suggests the magnitude of the impurities could be considered accurate to a factor of 3. The data are therefore most useful in comparing a series of operations. The only element which apparently varied in a completely random fashion was Al. Nowhere in the entire process did Al come in contact with the salt. Its origin, if not introduced during analysis, is unknown. The purified salt before crystal growth was the best material analyzed. Sublimation of the products of any stage of the purification increased the sodium content of the KCl. In general the iron content of the salt was increased during the crystal growth process. These points are illustrated in the data of Table I.

Table I

ARGON-ARC SPECTROGRAPHIC ANALYSIS OF POTASSIUM CHLORIDE[*]

RAW MATERIAL FOR SINGLE CRYSTALS				
	Fe	Na	Cu	Al
As Received	< 0.1	40.0	0.03	0.05
Ion Exchanged	< 0.1	2.1	0.02	0.04
Sublimed	0.5	8.3	0.04	0.09
SINGLE CRYSTALS				
As Received	1.9	10.0	0.07	0.12
Recrystallized	1.6	5.6	0.05	0.13
Chelex 100	0.3	1.8	0.03	0.14
Chelex 100 Sublimed	0.5	6.2	< 0.01	0.06
Chelex-Anion	0.1	2.6	0.02	0.04
Chelex-Anion Sublimed	0.7	5.4	< 0.01	0.21

Pb < 0.1 except 1 which had 0.1
V < 0.1 except 4 which had 1.9 and 5 which had 0.1
Ni < 1.0   Mo < 0.1   Cr < 1.0

*Data from Combustion Engineering, Inc.

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III INVESTIGATION OF CRYSTAL GROWTH FROM H_2S SOLVENT

The usual methods for growth of the electronically interesting cadmium and zinc sulfides is by high-temperature vapor-phase processes. Such techniques produce crystals of varying stoichiometry and strain. The success of hydrothermal systems with oxides suggested that if a proper solvent could be found, crystals other than oxides could be grown. In general the solubility of the compound is increased by operating the system at high temperatures while maintaining a suitable solvent density by application of pressure to the solution. The solvent system chosen was H_2S and various metal sulfides, the major effort being concentrated on CdS and ZnS.

A.   Experiments Using Pyrex and Quartz Containers

The properties of Pyrex or quartz such as chemical inactivity, easy handling, and avoidance of the many different leakage problems, made these materials the obvious choice for the container to use in our preliminary experiments. It is impossible to remove ZnS or CdS chemically from a stainless steel container without seriously corroding the container. The corrosive action of H_2S on stainless steel introduces additional impurities to the system and can also weaken the walls of the container by hydrogen embrittlement. For solubility measurements and crystal growing experiments, a 3 mm I.D. is the minimum requirement. This eliminated the use of capillary tubing which has maximum I.D. of 2 mm. The two most promising available standard heavy wall tubing were 9.5 mm O.D. - 5.5 mm I.D. Pyrex and 9.5 O.D. - 4.5 I.D. quartz.

The critical pressure, 1306 psi, critical density 0.348 g cm^{-3} and critical temperature, 100.4°C, of H_2S indicated that a working range up to 2000 psi, 104.5°C , corresponding to an H_2S density of 0.543 g cm^{-3}, would be sufficient for the first experiments.

Equipment was constructed to pressure-test the heavy wall tubing. (See Fig. 7). The results were most promising. The test specimens broke between 2500 and 3500 psi. The tubing itself never cracked, but

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BRASS HOLDER

TEFLON WASHER

USUAL BREAKING POINTS

WIDENED, STRENGTHENED END
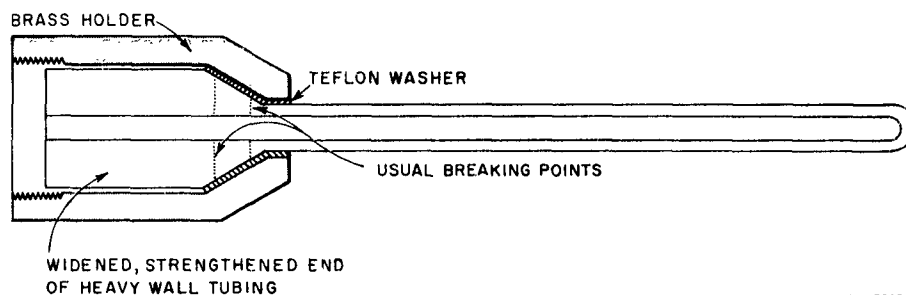OF HEAVY WALL TUBING

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FIG. 7 TUBING TEST CELL

always broke at the point where the brass holder exercised the "hold" on the tubing. As a result of these tests we conducted our first experiments in Pyrex and quartz.

The solubility of sulfides in H_2S was studied qualitatively using very thick-walled Pyrex "H" tubes (see Fig. 8), with glass wool filters. The "H" tubes were used for two kinds of measurements.

In the isopiestic experiments Sb_2S_3 was placed in one end of the "H" tube and CdS, PbS, or ZnS in the other end. The tubes and contents were dried on a vacuum line, and then H_2S was condensed on the dry salts to fill the tubes in the order of 20%. The tubes were placed in a constant temperature bath and kept there till equilibrium was achieved in the system (one or more days). H_2S evaporated from the Sb_2S_3 arm and recondensed in the CdS arm, indicating that the CdS is more soluble. In the case of the other two pairs (PbS - Sb_2S_3 and ZnS - Sb_2S_3) the results were inconsistent.

In the second type of H-tube experiment CdS (or ZnS, or PbS) was placed in one arm of the "H" tube, dried, and then H_2S was condensed. The temperature was slowly increased to achieve a single vapor phase of the H_2S in the container. The tubes were then kept at constant temperature and pressure to obtain a saturated solution of H_2S vapor in both arms. The "H" tubes were cooled down with dry ice and acetone
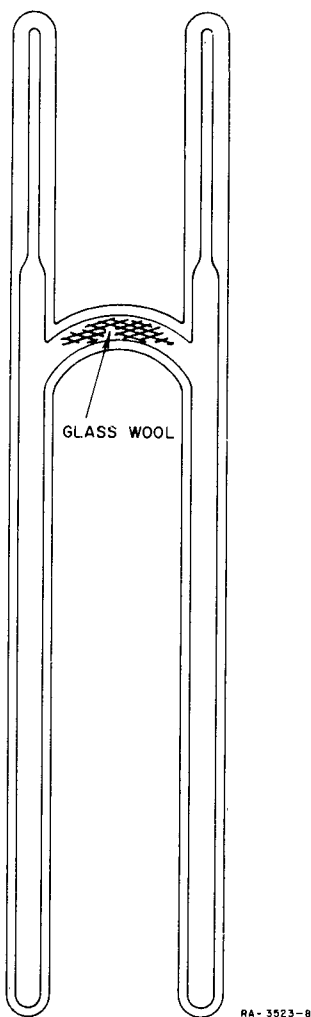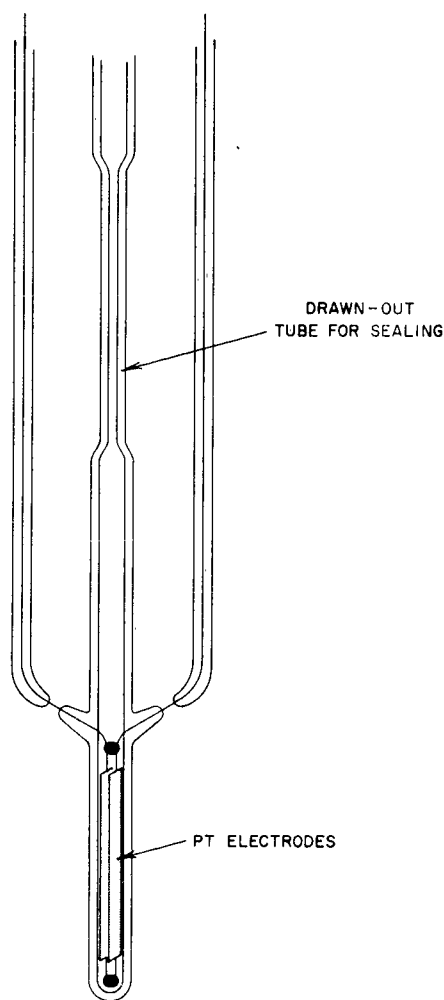
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FIG. 8 H-TUBE

GLASS WOOL

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before they were opened. After the
H_2S had evaporated, the "residue"
in the "empty" arm was dissolved in
acid and analyzed for Cd (Zn or Pb).

The "H" tubes contained the H_2S
satisfactorily at a temperature of
71°C, corresponding to a pressure of
788 psi (vapor pressure of H_2S).
However, they regularly failed around
the critical region of H_2S (100.4°C
and 1306 psi). Since it was necessary
for one end of the container to be
in liquid nitrogen while the container
was being sealed, it is possible that
strains developed in the walls and
were responsible for the failures at
these "low" pressures. The solubil-
ities at these temperatures and vapor
densities were very low. Since sol-
ubility should increase with an in-
crease in temperature and vapor
density, the experiments were continued
in a higher temperature-pressure-
density range. (At 137.6°C, and
0.7223 g cm^{-3} H_2S density for example,
the pressure is approximately 10,000
psi.)

Glass conductivity cells were
constructed with a 0.1 cm^{-1} cell
constant. In the temperature range
(below 65°C) where we could use them,
the conductivity of liquid H_2S

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DRAWN-OUT
TUBE FOR SEALING

PT ELECTRODES

RA-3523-9

FIG. 9 CONDUCTIVITY CELL

and CdS - H_2S or ZnS - H_2S solu-
tions was less than 10^{-8} mho (see
Fig. 9).

As our measurements indicated
that even at 70°C, some cadmium
sulfide was soluble, attempts were
made to grow crystals around this
temperature in a quartz tube, since
quartz could withstand the expected
pressures. CdS powder was placed
on the bottom of the tube and a
CdS seed crystal was located in
the upper part (approximately 4
inches higher). (Fig. 10). H_2S
was condensed in the quartz tube
which was then sealed off. The
lower part of the tube was placed
in a constant temperature bath (at
75°C) and the top of the tube was
insulated. A small temperature
gradient was achieved this way.
The process was too slow to have
any practical significance at 75°C
and at the H_2S density (0.2 g cm^{-3})
in these vessels.

B.   Examination of the H_2S-CdS and H_2S-ZnS Systems in High-Pressure
      Stainless Steel Autoclaves

The experiments were continued in stainless steel autoclaves.
Because of the dangers and experimental difficulties involved in hand-
ling H_2S and the leakage problems with these systems we chose to use
small (4 or 12 inches long, 10 or 30 ml volume) so-called test-tube
reactors with a guaranteed pressure range of 20,000 psi. Because of the

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GLASS WOOL
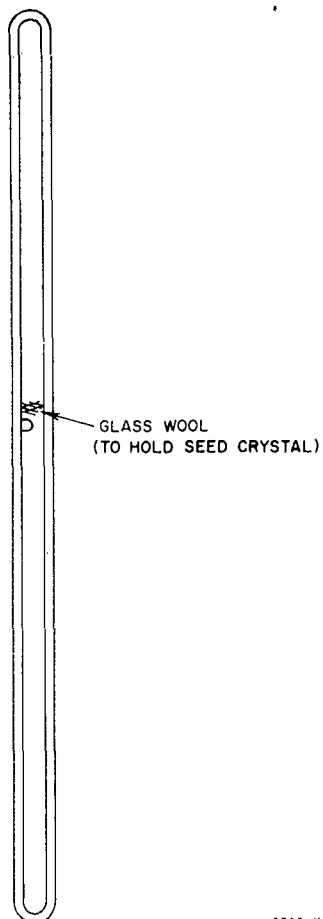(TO HOLD SEED CRYSTAL)

RA-3523-11

FIG. 10   SIMPLE CRYSTAL GROWING TUBE

simplicity, easy handling, and simple construction, an oil bath was used with a temperature range up to 170°C.

In the development of a new high-pressure steel system, which must work in a very broad temperature range (-196°C to +160°C), months are required to overcome difficulties which appear trivial in retrospect and to develop the proper technique. All such problems have been solved except one, the prevention of gas leakage through the electrical leads. The Teflon and MgO-coated platinum in a stainless steel tube gave the best results, but even this did not solve the main problem. At the pressure and temperature used, the leads developed H_2S leaks within a few days. Furthermore, the resistance of the lead was the same order or less than that of the H_2S solutions $(10^5 - 10^6 \ \Omega)$. It is believed that quartz-filled leads may be the answer to this problem, but no manufacturer produced such leads. As a result of our negotiations during the last four months, Pressure Products Inc. has agreed to manufacture such leads, but unfortunately none were available for the research program.

Experiments were also carried out with stainless steel and gold-plated autoclaves, and in this effort two autoclaves were gold-plated. In the experiments completed there was no recognizable advantage in the use of gold plating.

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A temperature-pressure curve of the ZnS-H_2S system was obtained at constant density. The conductivity of the solution was measured at the same time also to obtain information about the amount of ZnS dissolved. The pressure was measured with a 10,000 psi Astra gauge, which was connected to the autoclave through a gauge-protecting bellows. (See Fig. 11). The data are questionable since the system slowly leaked through the insulator in the electrical lead.
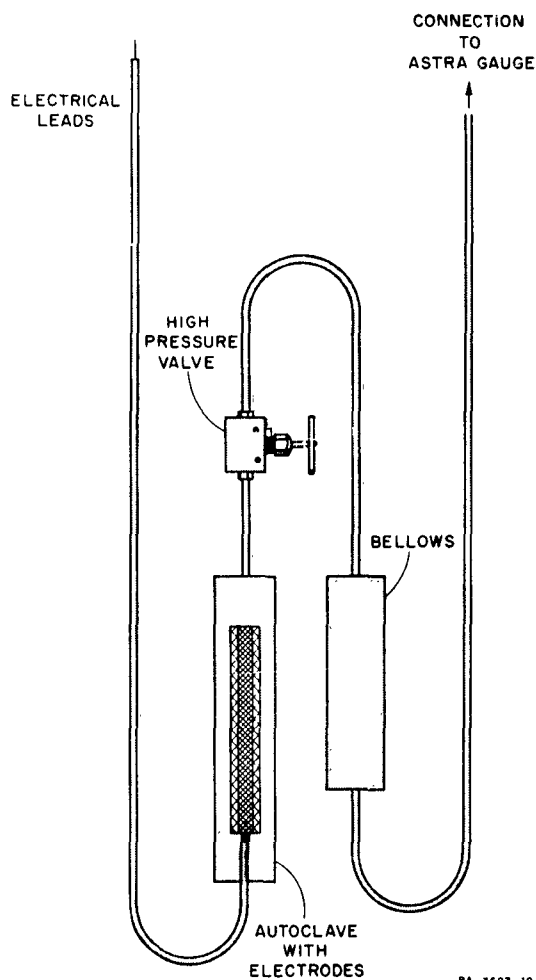

FIG. 11 STAINLESS STEEL SYSTEM

The solubility of ZnS was measured at 156°C and 5200 psi and found to be about 2 parts per million by weight. There was no time available to complete similar experiments and check the reliability of these data. The experimental setup and technique were similar to those used with Pyrex. (See Fig. 12).
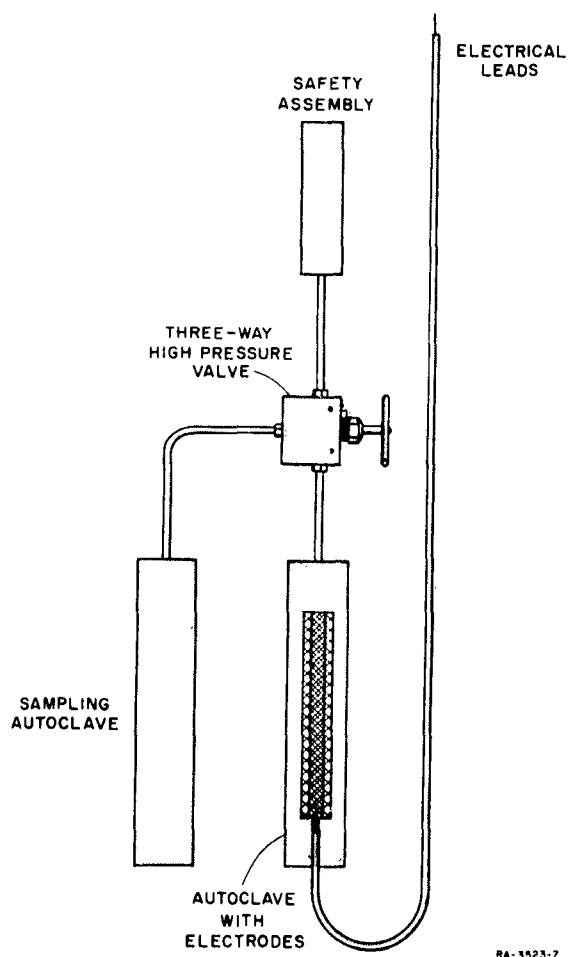

FIG. 12 STAINLESS STEEL SAMPLING SYSTEM

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Conductivity measurements were made in the same assemblies which were used for solubility measurements. The filling technique was the same as described earlier. The cell constants were approximately 0.016 cm^{-1}. A Model 250 ESI Universal impedance bridge was used at 1 KC and 5 KC with a variable capacitance box to measure the resistance of the ZnS solution. The results of a measurement with H_2S-ZnS system are shown on Fig. 13. One has to keep in mind, that because of the relatively low resistance of the lead in vacuum ($\sim 10^5 \ \Omega$), compared with the resistance of the cell ($10^5 - 10^6 \ \Omega$), the data have only a questionable meaning. Because of the leakage through the electrical lead, the density of the H_2S was not constant and was known only to within 5 to 10%. The change of conductivity with time at "constant"
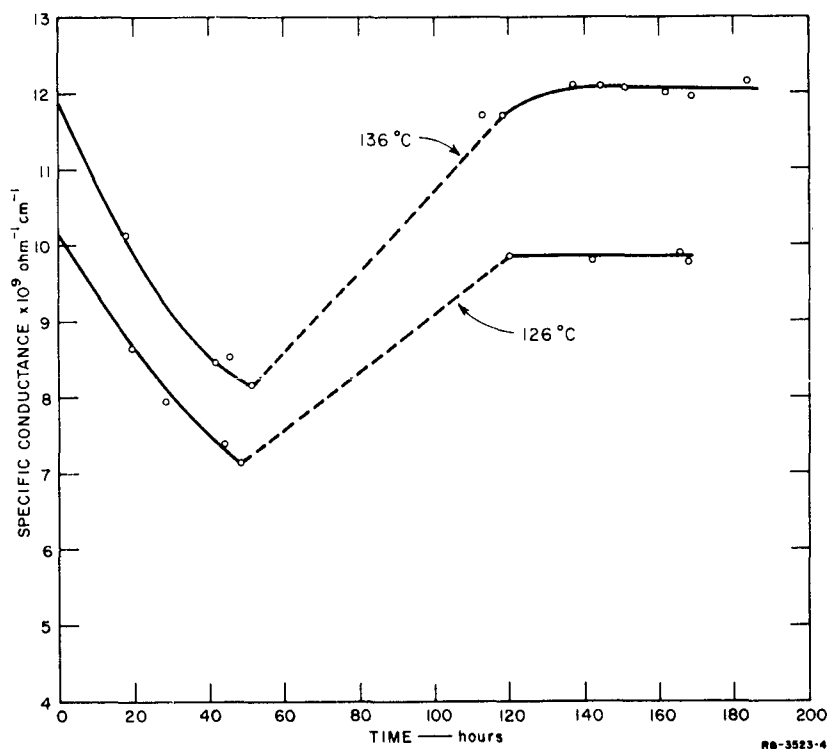

FIG. 13   SPECIFIC CONDUCTANCE OF ZnS in H_2S

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temperature and density can be interpreted in the following way:
During the first two days the conductivity dropped because we were
actually measuring the change in resistance of the insulation in the
electrical lead due to the removal of H_2O from the MgO insulation.
This resistance increased as a result of "drying" by heat and the
probable displacement of H_2O molecules by H_2S molecules. (To minimize
this effect the electrical leads were baked for several days at 110°C
before assembly.) The data obtained during the last 100 hours can be
interpreted in two different ways: (a) The conductivity of the solution
increased and dominated over the decreased conductivity of the insulation,
and therefore this part of the curve represents the conductivity of the
saturated ZnS-H_2S solution, this means it took approximately 5 days to
obtain a saturated solution. (b) It is also possible, that the reason
for the increase in conductivity was the leak of H_2S through the lead
and these points correspond to the conductivity of the H_2S filled insu-
lation.

One CdS-H_2S and one ZnS-H_2S crystal growing experiment were
completed. For these a twelve inch autoclave was used. In order to
establish a thermal gradient in the autoclave the oil bath was heated
from below and the autoclave allowed to protrude above the oil bath.
The seed crystals were located in the top end of the autoclave and the
powder was placed on the bottom. The seed crystals did not gain weight.
However, there was evidence of some mass transfer. Some tiny white and
yellowish crystals were found (see Fig. 14). X-ray analysis showed
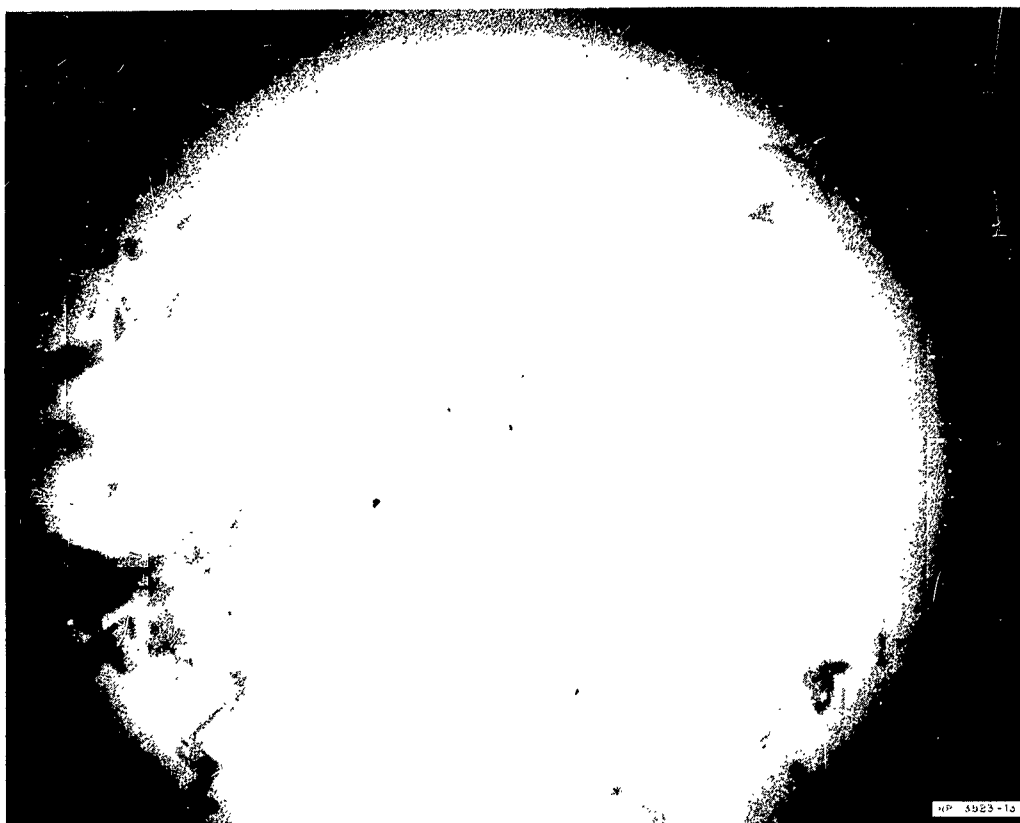that these were orthorhombic α sulfur crystals.

FIG. 14   ORTHORHOMIC – ⍺ SULFUR CRYSTALS

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IV CONCLUSIONS

The crystals grown from KCl purified by ion exchange are superior to commercial KCl crystals. The OH⁻ concentration can be reduced significantly by drying techniques used in this program. The sodium content and probably the bromide content can be reduced. The divalent ion concentration, if compensation does not occur, is comparable to the 10-zone pass material of Gründig. In general the met.od shows great promise for the purification of relatively large amounts of KCl for single crystal growth. The results of this investigation have been reported at the 1962 International Color Center Symposium at Stuttgart, Germany.

The study of crystal growth from supercritical H_2S solutions was hampered by the need to develop satisfactory experimental techniques and equipment. One of the major problems was the leakage of H_2S through the compressed powder insulation of the electrical leads. Apparently this can be solved, and, time permitting, would have been, by leads using solid insulators. The results that were obtained indicate that the H_2S-CdS and H_2S-ZnS systems may prove valuable for growth of crystals of the sulfides, although more research will be required to develop practical systems.

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